Rapidly Crosslinkable DOPA containing Terpolymer Adhesives and PEG-based Crosslinkers for Biomedical Applications

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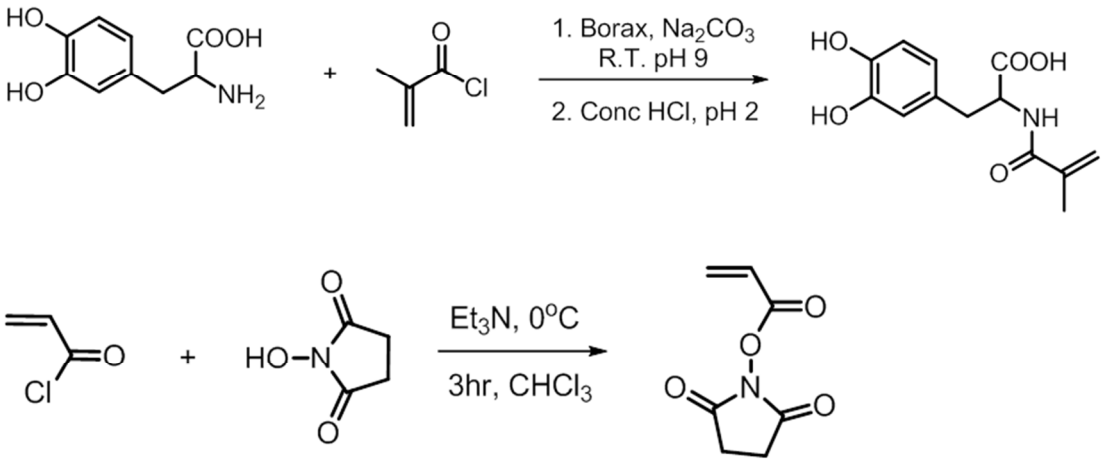
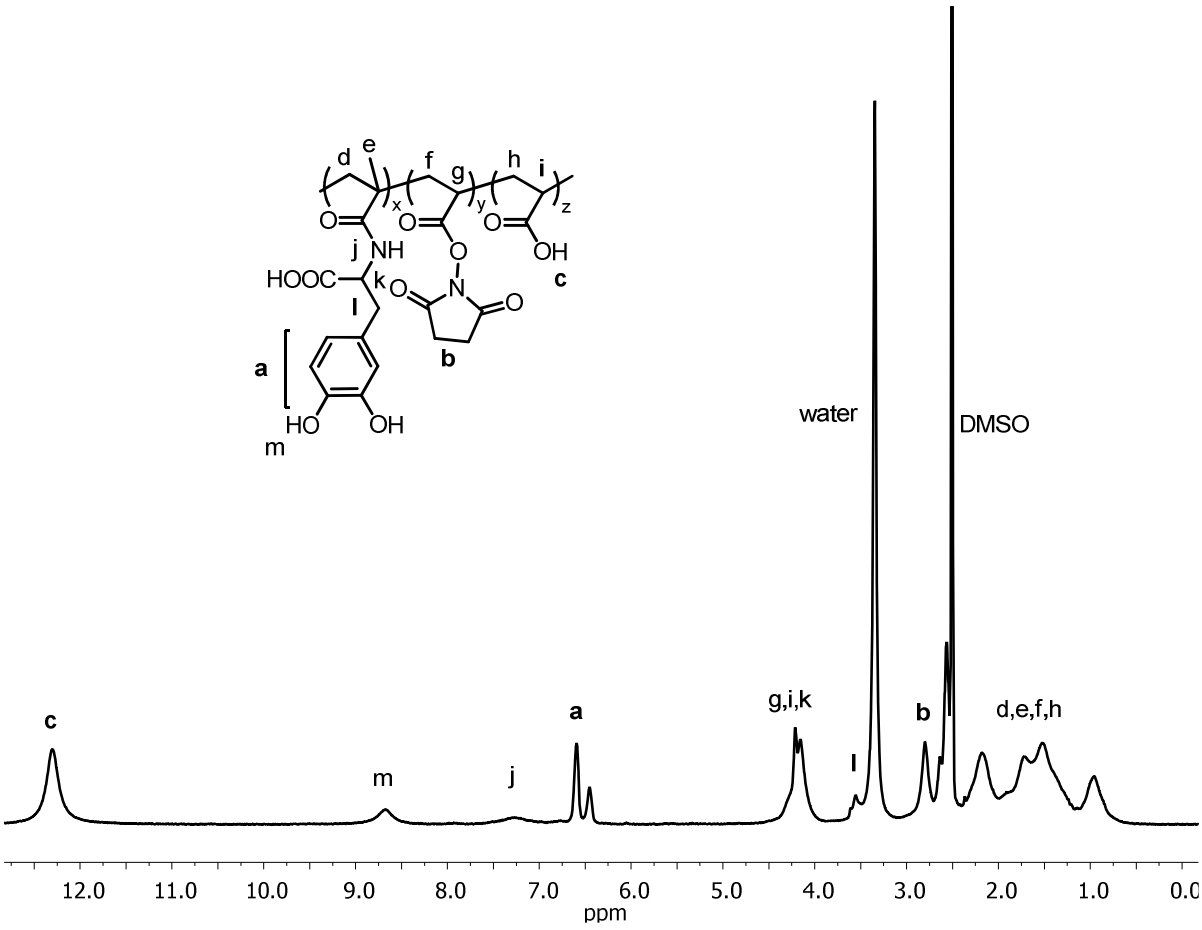
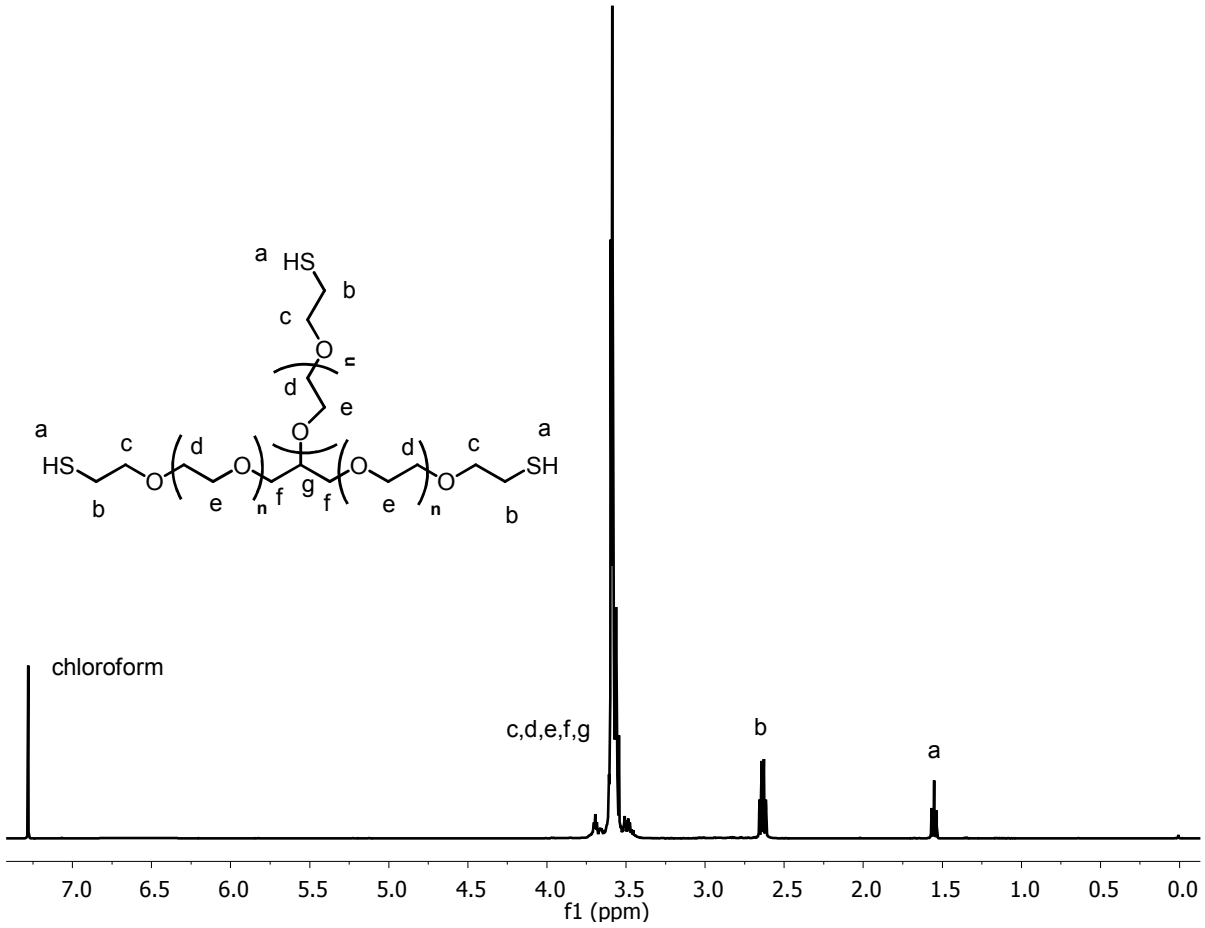
Supporting information



Scheme S1. Synthesis of vinyl monomers for adhesive polymerization


d
e
f
g
h
i
x
y
z
O
NH
j
k
l
HOOC
N
a
b
c
m
HO
OH
water
DMSO
g,i,k
d,e,f,h
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


a
HS
b
c
O
n
d
e
a
HS
c
d
O
O
d
c
a
SH
b
e
n
f
g
f
e
n
b
chloroform
c,d,e,f,g
b
a
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

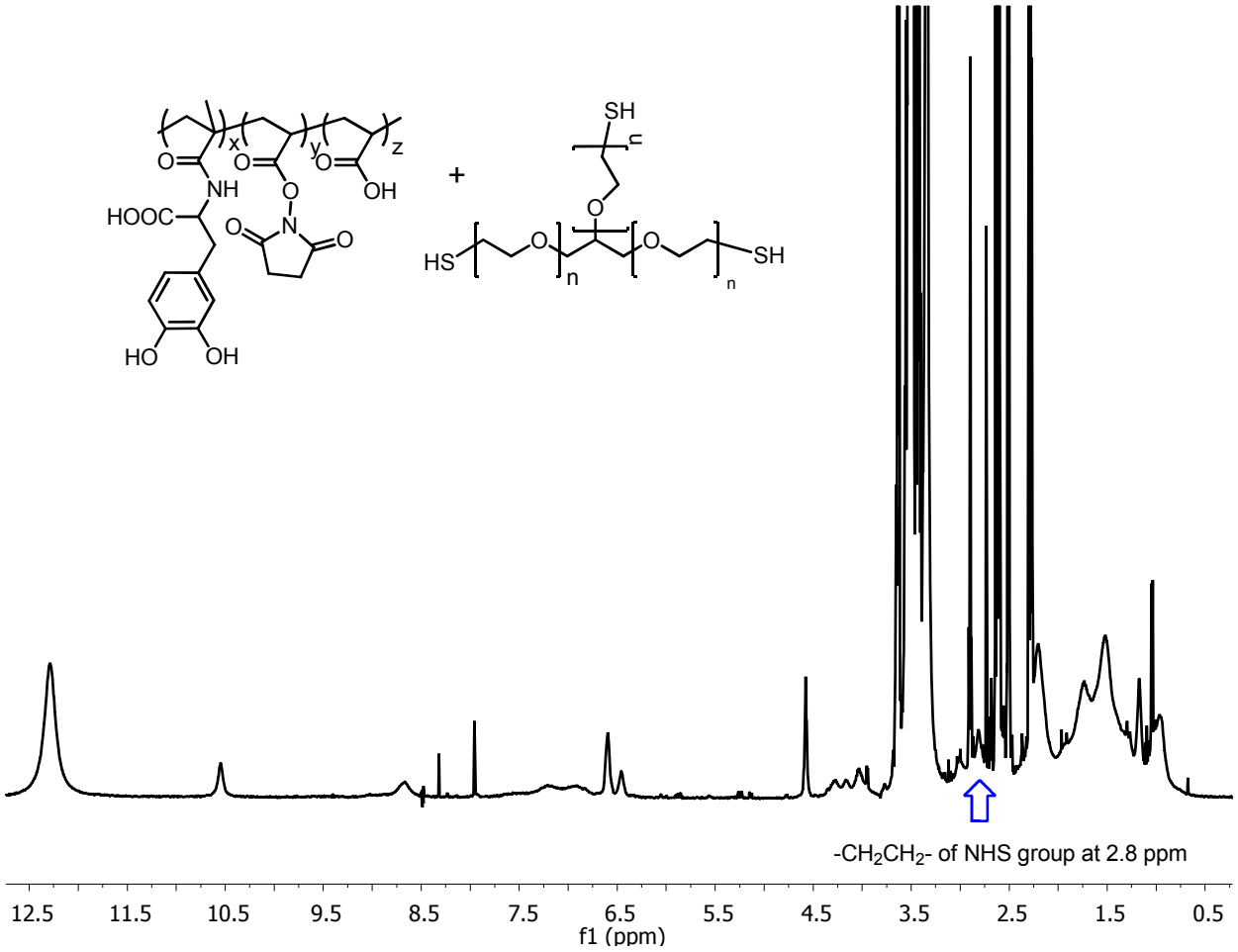
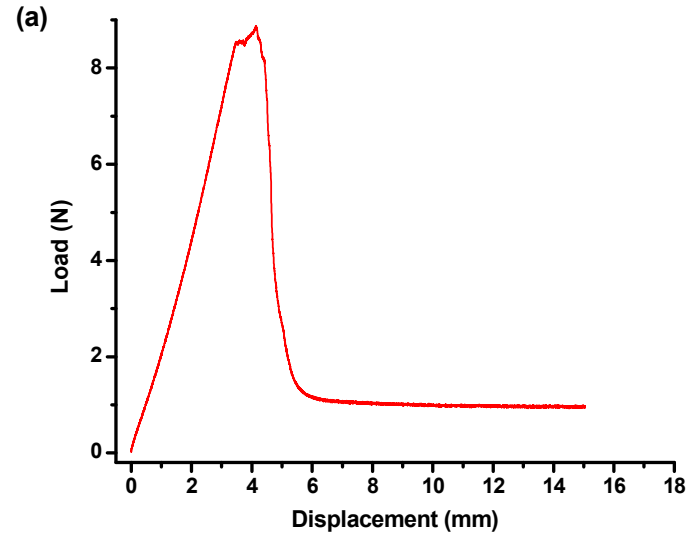
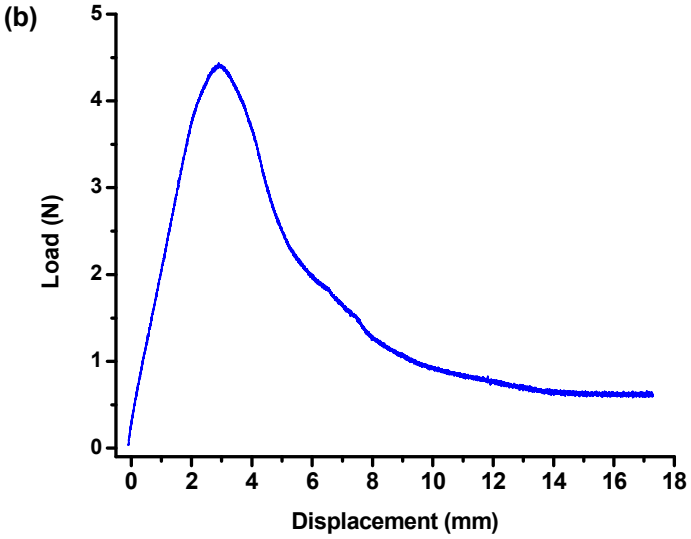


Figure S1. ^{1}H NMR spectra of adhesive, poly(AA-co-AANHS-co-MDOPA) in DMSO-d6 (top), crosslinker, thiol PEG in $CDCl_3$ (middle) and mixture of poly(AA-co-AANHS-co-MDOPA) and thiol PEG in DMSO-d6 (bottom). In poly(AA-co-AANHS-co-MDOPA) and thiol PEG mixture ^{1}H NMR, -CH_2CH_2- integration (2.8 ppm) of N-hydroxysuccinimide ester (NHS) groups were significantly decreased compared to pure poly(AA-co-AANHS-co-MDOPA)'s ^{1}H NMR. This integration changes demonstrate crosslinking between poly(AA-co-AANHS-co-MDOPA) and crosslinker, thiol PEG by showing consumption of NHS functionality.


(a)
Load (N)
0
2
4
6
8
0
2
4
6
8
10
12
14
16
18
Displacement (mm)


(b)
Load (N)
0
1
2
3
4
5
0
2
4
6
8
10
12
14
16
18
Displacement (mm)

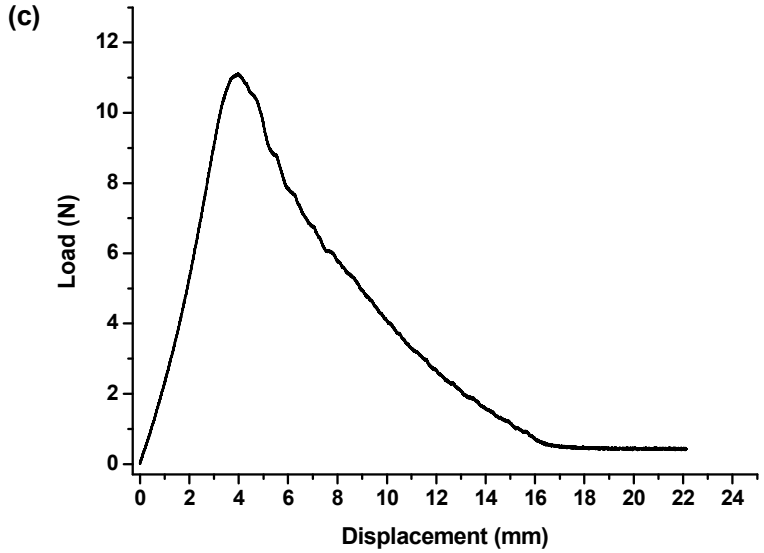


Figure S2. Load vs. displacement plot of (a) crosslinked adhesive, (b) uncrosslinked adhesive and (c) Super Glue from lap shear strength tests; crosslinked adhesive shows much sharper failure of load than uncrosslinked adhesive.

Additional series of lap shear strength tests were performed at 5 mm/mins constant cross head speed. Detail test condition is described in experimental section. Poly(AA-co-AANHS) demonstrated 0.85 ± 0.11 kPa of maximum adhesion strength. Poly(AA-co-AANHS-co-MDOPA) was 3.14 ± 0.70 kPa and crosslinked adhesive, Mixture of poly(AA-co-AANHS-co-MDOPA) and thiol PEG, showed 6.220 ± 1.08 kPa. Super glue's maximum adhesion strength was 14.09 ± 2.27 kPa.